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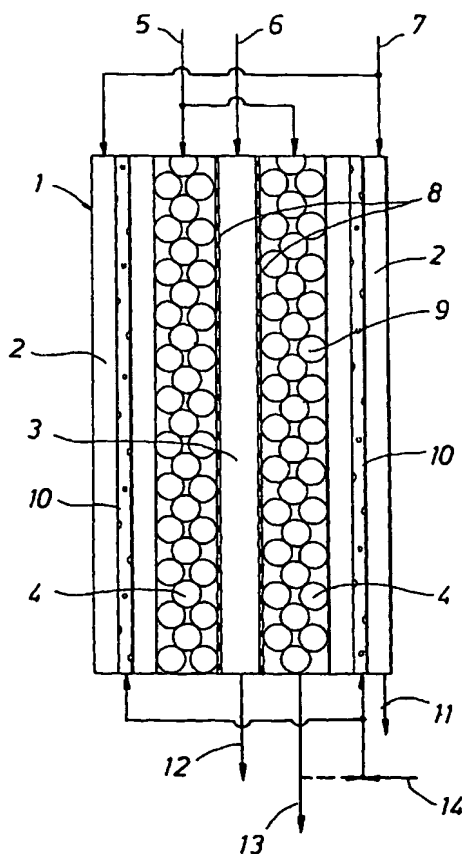
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[Continued on next page]

(54) Title: APPARATUS AND PROCESS FOR PRODUCTION OF HIGH PURITY HYDROGEN



(57) Abstract: The invention relates to a new and improved process and ap-  
paratus for the production of high purity hydrogen by steam reforming. The  
apparatus is an integrated flameless distributed combustion-membrane steam  
reforming (FDC-MSR) or reactor for steam reforming of a vaporizable hydro-  
carbon to produce H<sub>2</sub> and CO<sub>2</sub>, with minimal CO, and minimal CO in the H<sub>2</sub>  
stream. The flameless distributed combustion drives the steam reforming reac-  
tion which pro-vides great improvements in heat exchange efficiency and load  
following capabilities. The reactor may contain multiple flameless distributed  
combustion chambers and multiple hydrogen-selective, hydrogen-permeable,  
membrane tubes. The feed and reaction gases may flow through the reac-  
tor either radially or axially. A further embodiment of the invention involves  
producing high purity hydrogen by dehydrogenation using an integrated FDC  
-membrane de-hydrogenation reactor. A still further embodiment of the in-  
vention involves a zero emission hybrid power system wherein the produced  
hydrogen is used to power a high-pressure internally manifolded molten car-  
bonate fuel cell. In addition, the design of the FDC-SMR powered fuel cell  
makes it possible to capture good concentrations of CO<sub>2</sub> for sequestration or  
use in other processes.

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European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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(84) **Designated States (regional):** ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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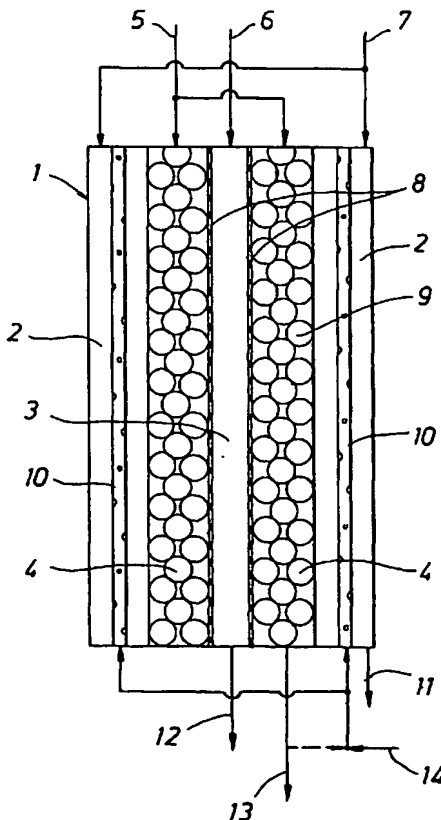
(72) Inventors; and

(75) Inventors/Applicants (for US only): **MATZAKOS, Andreas, Nicholas** [US/US]; 2115 Parkview Lane, Missouri City, TX 77459 (US). **WELLINGTON, Scott, Lee** [US/US]; 5109 Aspen Street, Bellaire, TX 77401 (US). **CLOMBURG, Lloyd, Anthony** [US/US]; 18207 Widcombe Drive, Houston, TX 77084 (US). **VEENSTRA, Peter** [US/US]; 8507 Chipping Rock Drive, Sugar Land, TX 77479 (US). **MUNSHI, Abdul, Wahid** [US/US]; 12635 S. Dairy Ashford, Houston, TX 77099 (US). **JEAN, Rong-her** [US/US]; 5810 Wilkins Lane, Sugar Land, TX 77479 (US). **ELLIOTT, Glenn, William** [US/US]; 148 Westover Drive, Akron, OH 44313 (US). **GROEN-EVELD, Michiel, Jan** [NL/NL]; Volmerlaan 8, NL-2288 GD, Rijswijk, NL-2288 The Netherlands (NL).

(74) Agent: **TSANG, Y., Grace**; **SHELL OIL COMPANY**, One Shell Plaza, P.O. Box 2463, Houston, TX 77252-2463 (US).

[Continued on next page]

(54) Title: APPARATUS AND PROCESS FOR PRODUCTION OF HIGH PURITY HYDROGEN



(57) Abstract: The invention relates to a new and improved process and apparatus for the production of high purity hydrogen by steam reforming. The apparatus is an integrated flameless distributed combustion-membrane steam reforming (FDC-MSR) or reactor for steam reforming of a vaporizable hydrocarbon to produce  $H_2$  and  $CO_2$ , with minimal  $CO$ , and minimal  $CO$  in the  $H_2$  stream. The flameless distributed combustion drives the steam reforming reaction which provides great improvements in heat exchange efficiency and load following capabilities. The reactor may contain multiple flameless distributed combustion chambers and multiple hydrogen-selective, hydrogen-permeable, membrane tubes. The feed and reaction gases may flow through the reactor either radially or axially. A further embodiment of the invention involves producing high purity hydrogen by dehydrogenation using an integrated FDC-membrane de-hydrogenation reactor. A still further embodiment of the invention involves a zero emission hybrid power system wherein the produced hydrogen is used to power a high-pressure internally manifolded molten carbonate fuel cell. In addition, the design of the FDC-SMR powered fuel cell makes it possible to capture good concentrations of  $CO_2$  for sequestration or use in other processes.



(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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## WE CLAIM:

1. A flameless distributed combustion heated, membrane,  
5 steam reforming reactor comprising:
  - a) a reforming chamber containing a reforming catalyst  
bed, said reforming chamber having an inlet for vapor-  
10 izable hydrocarbon and steam, a flow path for hydrogen  
and by-product gases resulting from the reforming reac-  
tions taking place in said reforming chamber and an  
outlet for said by-product gases,
  - b) at least one flameless distributed combustion cham-  
ber in a heat transferring relationship with said re-  
forming catalyst bed whereby a distributed, controlled  
15 heat flux is provided by said flameless distributed  
combustion chamber to said reforming catalyst bed, said  
flameless distributed combustion chamber comprising an  
inlet and a flow path for an oxidant, an outlet for  
combustion gas and further comprising a fuel conduit  
20 having an inlet for fuel and a plurality of fuel noz-  
zles which provide fluid communication from within the  
fuel conduit to the flow path of said oxidant, said  
plurality of fuel nozzles being sized and spaced along  
the length of said fuel conduit so that no flame re-  
25 sults when said fuel is mixed with said oxidant in said  
flameless distributed combustion chamber;
  - c) a preheater capable of preheating said oxidant to a  
temperature that when said fuel and said oxidant are  
mixed in said flameless distributed combustion chamber,  
30 the temperature of the resulting mixture of said oxi-  
dant and fuel exceeds the autoignition temperature of  
said mixture; and
  - d) at least one hydrogen-selective, hydrogen-  
permeable, membrane tube in contact with said reform-

ing catalyst bed, said membrane tube having an outlet whereby hydrogen formed in the reforming chamber permeates into said membrane tube and passes through said outlet.

- 5 2. A process for the production of hydrogen, comprising:
- a) reacting steam with a vaporizable hydrocarbon at a temperature of from about 200°C to about 700°C and at a pressure of from about 1 bar to about 200 bar in a reaction zone containing a reforming catalyst to produce
- 10 a mixture of primarily hydrogen and carbon dioxide, with a lesser amount of carbon monoxide;
- b) providing heat to said reaction zone by employing at least one flameless distributed combustion chamber thereby driving said reaction; and
- 15 c) conducting said reaction in the vicinity of at least one hydrogen-permeable, hydrogen-selective membrane tube, whereby hydrogen formed in said reaction zone permeates through said hydrogen selective membrane tube and is separated from said carbon dioxide and carbon
- 20 monoxide.
3. A membrane, steam reforming reactor comprising:
- a) a reforming chamber containing a reforming catalyst bed, said reforming chamber having an inlet for vaporizable hydrocarbon and steam, a flow path for hydrogen
- 25 and by-product gases resulting from the reforming reactions taking place in said reforming chamber and an outlet for said by-product gases,
- b) at least one combustion chamber in a heat transferring relationship with said reforming catalyst bed,
- 30 and
- c) at least one hydrogen-selective, hydrogen-permeable, membrane tube in contact with said reforming catalyst bed, and the membrane tube is also connected to a section containing a metal hydride precursor, and the hydrogen formed

in the reforming chamber permeates through said membrane tube to said section containing the metal hydride precursor which reacts with the permeated hydrogen to form hydride.

4. A flameless distributed combustion heated, membrane,

5 dehydrogenation reactor comprising:

a) a dehydrogenation chamber containing a catalyst bed, said dehydrogenation chamber having an inlet for vaporizable hydrocarbon, a flow path for hydrogen and product gases resulting from the dehydrogenation reactions taking place in said dehydrogenation chamber and an outlet for said product gases,

b) at least one flameless distributed combustion chamber in a heat transferring relationship with said catalyst bed whereby a distributed, controlled heat

15 flux is provided by said flameless distributed combustion chamber to said catalyst bed, said flameless distributed combustion chamber comprising an inlet and a flow path for an oxidant, an outlet for combustion gas

and further comprising a fuel conduit having an inlet for fuel and a plurality of fuel nozzles which provide fluid communication from within the fuel conduit to the flow path of said oxidant, said plurality of fuel nozzles being sized and spaced along the length of said fuel conduit so that no flame results when said fuel is

25 mixed with said oxidant in said flameless distributed combustion chamber;

c) a preheater capable of preheating said oxidant to a temperature that when said fuel and said oxidant are mixed in said flameless distributed combustion chamber, the temperature of the resulting mixture of said oxidant and fuel exceeds the autoignition temperature of said mixture; and

30 d) at least one hydrogen-selective, hydrogen-permeable, membrane tube in contact with said catalyst

bed, said membrane tube having an outlet whereby hydrogen formed in the dehydrogenation chamber permeates into said membrane tube and passes through said outlet.

5. A process for dehydrogenation of ethylbenzene, which  
5 process comprises the steps of feeding ethylbenzene into the reactor as described in Claim 4 to produce styrene and hydrogen.
6. A hydrogen fuel cell, wherein the hydrogen feed is made by a process as described in claims 2 or 5.
- 10 7. The reactor, process or fuel cell of claims 1, 2, 3, 4, or 5, wherein said catalyst bed is in contact with multiple hydrogen-selective, hydrogen-permeable membrane tubes.
8. The reactor, process or fuel cell of claims 1, 2, 3, 4, 5, 6, or 7, wherein said catalyst bed is in heat transferring contact with multiple flameless distributed combustion  
15 chambers.
9. The reactor, process or fuel cell of claims 1 - 8, wherein the vaporizable hydrocarbon and steam flow axially through said catalyst bed.
- 20 10. The reactor process or fuel cell of claims 1-8, wherein the vaporizable hydrocarbon and steam flow radially through said catalyst bed.
11. The reactor, process or fuel cell of claims 1-8, wherein a sweep gas is used to promote the diffusion of hydrogen through said membrane tube, said sweep gas being selected from the group consisting of steam, carbon dioxide, nitrogen and condensable hydrocarbon and the vaporizable hydrocarbon is selected from the group consisting of natural gas, methane, ethyl benzene, methanol, ethane, ethanol,  
25 propane, butane, light hydrocarbons having 1-4 carbon atoms in each molecule, light petroleum fractions including naphtha, diesel, kerosene, jet fuel or gas oil, and hydrogen, carbon monoxide and mixtures thereof.
- 30



12. The reactor, process or fuel cell of claims 1-11 wherein the ratio of the surface area of said flameless distributed combustion chambers to the surface area of said membrane tubes is from about 0.1 to about 20.0, particularly from about 0.2 to about 5.0, more particularly from about 0.5 to about 5.0, and still more particularly from about 0.3 to about 3.0 and even more particularly from about 1.0 to about 3.0.

13. The reactor, process or fuel cell of claims 1-12 wherein said catalyst bed contains baffles in a form selected from the group consisting of (i) washers and disks, and (ii) truncated disks.

14. The reactor, process or fuel cell of claims 1-13, wherein the hydrogen-selective and hydrogen-permeable membrane is made of a Pd-alloy layer supported on a porous metal, particularly a Pd-alloy layer deposited by electroless plating on porous metal with an in-situ oxide protection layer.

15. The reactor, process or fuel cell of claims 1-13, wherein the hydrogen-selective and hydrogen-permeable membrane is made of a Pd-alloy layer supported on a porous metal selected from the group consisting of (i) porous nickel-based alloy, (ii) porous Hastelloy®, and (iii) porous Inconel.

16. The reactor, process or fuel cell of claims 1-13, wherein the hydrogen-selective and hydrogen-permeable membrane has a ratio of length to diameter of less than about 500, gaps between the membrane tubes are from about  $\frac{1}{4}$  inch (about 0.64 cm) to about 2 inches (about 5.08 cm), and gap between the membrane and FDC tubes is from about  $\frac{1}{4}$  inch (about 0.64 cm) to about 2 inches (about 5.08 cm).

17. The reactor, process or fuel cell of claims 1-13, wherein the hydrogen-selective and hydrogen-permeable membrane has a ratio of length to diameter of less than about

250, gap between the membrane tubes is from about  $\frac{1}{2}$  inch (about 1.27 cm) to about 1 inch (about 2.54 cm), and gap between the membrane and FDC tubes is from about  $\frac{1}{2}$  inch (about 1.27 cm) to about 1 inch (about 2.54 cm).

5 18. The reactor, process or fuel cell of claims 1-17, wherein the FDC chamber having an external tubular dimension such that the length to diameter ratio is higher than 4.

10 19. The reactor, process or fuel cell of claims 1-17, wherein the FDC chamber having a tubular dimension such that the length to diameter ratio is higher than 10.

20. The reactor, or process of claims 1-3, wherein carbon dioxide produced from said steam reforming chamber has a pressure of from about 0.1 to about 20 MPa, particularly  
15 from about 1 to about 5 MPa based on an international standard.

21. The reactor or process of claims 1-3, wherein carbon dioxide produced from said steam reforming chamber has a concentration of from about 80% to about 99% molar dry ba-  
20 sis.

22. The reactor, process, or fuel cell of claims 1-3, wherein carbon dioxide produced from said steam reforming chamber has a concentration of from about 90% to about 95% molar dry basis.

25 23. The reactor, process, or fuel cell of claims 1-3, wherein carbon dioxide produced from, said steam reforming chamber is used at least in part for enhanced recovery of oil in oil wells or enhanced recovery of methane in coal bed methane formations.

30

**STATEMENT UNDER ARTICLE 19(1)**

The amended claims 1, 2, 3, 4, 11, 14, 15, 16, 17 and 21; as well as the unchanged claims 5, 6, 7, 8, 9, 10, 12, 13, 18, 19, 20, 22, and 23 are all directed to a process or a reaction comprising:

- (a) a reaction zone containing a reforming catalyst to produce a mixture of hydrogen and carbon dioxide,
- (b) providing heat to said reaction zone by employing at least one flameless distributed combustion chamber (that is, the fuel is provided by "distributed" fuel injection), and
- (c) conducting the reaction in the vicinity of at least two hydrogen-permeable, hydrogen selective membrane tubes.

**Unity of Invention**

Applicants believe that by the amendments submitted herewith, the requirement of unity of invention is fulfilled in the group of inventions of claims 1-23. This is because each of the inventions in claims 1-23 comprises the special technical features of the combination of (i) employing multiple hydrogen permeable and selective tubes and (ii) providing heat by "distributed" injection of fuel employing a flameless distributed combustion chamber, which contributes technically over the prior art. It follows that the inventions of claims 1-23, as linked by the afore-mentioned common inventive technical features, forms a single inventive concept within the meaning of Rule 13.1 PCT.

**Novelty and Inventive Steps**

By the amendments submitted herewith, Applicants believe that claims 1-23 are novel and inventive over the prior art cited in the International Search Report.

The present claims 1-23 relate to an apparatus and process for providing controlled heat to a process for producing hydrogen, which process is conducted in a process chamber heated with "distributed injection" of fuel in the heater to result in a distributed exothermic heat release. This results in the advantage of providing a controllable heat flux and uniform controllable temperature profile to the process chamber.

Furthermore, the claims are amended to clearly define that the inventive system employs multiple hydrogen permeable and selective tubes to produce high purity hydrogen in high yield.

5            Claims 1-23 are novel and inventive over WO 02/070402 and WO 99/19302 cited in the International Search Report, because these references do not require the use of multiple hydrogen selective tubes as employed in the presently claimed inventions. It is to be noted that WO 02/070402 is published prior to the international filing date of this patent application but later than the priority date.

10

Claims 1-23 are further distinguishable over EP1,024,111, EP924,126 and US5,861,137, which use oxidation chamber packed with catalyst, for the following reasons:

- 15            (a)        In the present claimed invention employs a heater system with distributed injection of fuel; fuel is not premixed or uncontrollably mixed with the air or oxygen as provided in these three references. The present system thus avoids the formation of hot spot which can damage the reactor, catalyst, hydrogen selective membranes, etc.
- 20            (b)        The present heater of distributed injection of fuel allows the heat flux profile to be designed by the nozzle (opening) locations and sizes, while the oxidation chamber packed with catalyst of these three references are not controlled in the distributed manner of the present inventions.
- (c)        The present heater does not require the use of catalyst for combustion/oxidation in the heater.
- 25            (d)        The present heater may experience less pressure drop, thus involve less compression costs for the air and fuel than the designs of the three references.
- (e)        The heater design of the present invention has the advantages in reducing the maximum skin temperature of the heater and providing heat integration between inlet and outlet streams (air and flue gas).
- 30

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/27995

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01B3/38 C01B3/50 C01B3/48 C01B3/32 B01J19/24  
 B01J8/06 C07C5/333 H01M8/06 C01B31/20

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B B01J C07C H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC, COMPENDEX

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 02/070402 A (SHELL CANADA LTD ; SHELL INT RESEARCH (NL)) 12 September 2002 (2002-09-12) the whole document	1, 2, 4, 6-11, 14, 15, 20-23
X	EP 1 024 111 A (CHINESE PETROLEUM CORP) 2 August 2000 (2000-08-02) paragraph '0002! paragraph '0009! - paragraph '0013! paragraph '0018! paragraph '0027! claims figures 2-4	2, 3, 6
Y	same passages	1, 4, 7-11, 14, 15, 20-23
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&\* document member of the same patent family

Date of the actual completion of the international search

5 May 2004

Date of mailing of the international search report

10.05.04

Name and mailing address of the ISA

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Harf-Bapin, E

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/27995

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 99/18392 A (SHELL CANADA LTD ;SHELL INT RESEARCH (NL)) 15 April 1999 (1999-04-15)  page 15, line 33 -page 17, line 30 claims figures	1,4, 7-11,14, 15,20-23
X	same passages	5
A	----- PATENT ABSTRACTS OF JAPAN vol. 012, no. 160 (M-697), 14 May 1988 (1988-05-14) & JP 62 279264 A (MAZDA MOTOR CORP), 4 December 1987 (1987-12-04) abstract	3
X	----- EP 0 924 162 A (DBB FUEL CELL ENGINES GMBH) 23 June 1999 (1999-06-23) paragraph '0016!	6
A	paragraph '0012! - paragraph '0014!; figure 1	1-4
X	----- US 5 861 137 A (EDLUND DAVID J) 19 January 1999 (1999-01-19) figure 1	6
A	the whole document	1-4
A	----- US 5 229 102 A (MINET RONALD G ET AL) 20 July 1993 (1993-07-20) the whole document	1-4
A	----- PATENT ABSTRACTS OF JAPAN vol. 013, no. 532 (C-659), 28 November 1989 (1989-11-28) & JP 01 219001 A (HIDEKAZU KIKUCHI), 1 September 1989 (1989-09-01) abstract	1-4
A	----- ZIAKA Z D ET AL: "A HIGH TEMPERATURE CATALYTIC MEMBRANE REACTOR FOR PROPANE DEHYDROGENATION" JOURNAL OF MEMBRANE SCIENCE, ELSEVIER SCIENTIFIC PUBL.COMPANY. AMSTERDAM, NL, vol. 77, no. 2 / 3, 4 March 1993 (1993-03-04), pages 221-232, XP000387938 ISSN: 0376-7388 the whole document	5

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 03/27995

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

## 1. Claims: 1,4,5,6-23 (part.)

A membrane reactor for the production of hydrogen and by-products comprising:

- a) a process chamber containing a catalyst bed, having a inlet for gases such as vaporizable hydrocarbon and steam, a flow path for hydrogen and by-product gases resulting from the reactions taking place in the process chamber and an outlet for said by-product gases,
  - b) a flameless distributed combustion chamber in heat exchange relationship with said catalyst bed, said flameless distributed combustion chamber comprising an inlet and a flow path for an oxidant, an outlet for combustion gas and a fuel conduit having an inlet for fuel, a plurality of fuel nozzles providing fluid communication from the interior of the fuel conduit to the oxidant flow path and being spaced and sized so that no flame results,
  - c) a preheater suitable for preheating the oxidant,
  - d) at least one hydrogen-selective, hydrogen-permeable, membrane tube in contact with said catalyst, said membrane tube having an outlet for the hydrogen formed in the reforming chamber which permeates through the membrane.
- A process using said membrane reactor for the dehydrogenation of ethylbenzene into hydrogen and styrene is also claimed.

## 2. Claims: 2,6 (part.)

A process for the production of hydrogen, comprising:

- a) reacting steam with a vaporizable hydrocarbon in a reaction zone containing a reforming catalyst to produce a mixture of hydrogen and carbon dioxide and some carbon monoxide,
- b) providing heat to said reaction zone by employing at least one flameless distributed combustion chamber,
- c) conducting the reaction in the vicinity of at least one hydrogen-permeable, hydrogen selective membrane tube, whereby the hydrogen formed in said reaction permeates through said hydrogen-selective membrane tube and is separated from the carbon oxides.

## 3. Claims: 3,7-23 (part.)

A membrane reactor comprising:

- a) a process chamber containing a catalyst bed, said chamber having an inlet for vaporizable hydrocarbon and steam, a flow path for hydrogen and by-product gases resulting from the reactions taking place in the process chamber and an outlet for said by-product gases,
- b) at least one combustion chamber in heat exchange



FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

relationship with said catalyst bed,  
c) at least one hydrogen-selective, hydrogen-permeable,  
membrane tube in contact with said catalyst, said membrane  
tube being also connected to a section containing a metal  
hydride precursor.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/27995

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## PATENT COOPERATION TREATY

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PCT

NOTIFICATION OF THE RECORDING  
OF A CHANGE(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

TSANG, Y., Grace  
SHELL OIL COMPANY  
One Shell Plaza  
P.O. Box 2463  
Houston, TX 77252-2463  
United States of America

Date of mailing (day/month/year) 20 October 2004 (20.10.2004)	<b>IMPORTANT NOTIFICATION</b>
Applicant's or agent's file reference TH2244-PCT	
International application No. PCT/US2003/027995	International filing date (day/month/year) 05 September 2003 (05.09.2003)

1. The following indications appeared on record concerning:	
<input checked="" type="checkbox"/> the applicant	<input checked="" type="checkbox"/> the inventor <input type="checkbox"/> the agent <input type="checkbox"/> the common representative
Name and Address VEENSTRA, Peter 8507 Chipping Rock Drive Sugar Land, TX 77479 United States of America	State of Nationality US
	State of Residence US
	Telephone No.
	Facsimile No.
2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:	
<input type="checkbox"/> the person <input type="checkbox"/> the name <input type="checkbox"/> the address <input checked="" type="checkbox"/> the nationality <input type="checkbox"/> the residence	
Name and Address VEENSTRA, Peter 8507 Chipping Rock Drive Sugar Land, TX 77479 United States of America	State of Nationality NL
	State of Residence US
	Telephone No.
	Facsimile No.
3. Further observations, if necessary:	
4. A copy of this notification has been sent to:	
<input checked="" type="checkbox"/> the receiving Office	<input type="checkbox"/> the designated Offices concerned
<input type="checkbox"/> the International Searching Authority	<input checked="" type="checkbox"/> the elected Offices concerned
<input checked="" type="checkbox"/> the International Preliminary Examining Authority	<input type="checkbox"/> other:

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Kinam HA
Facsimile No. (41-22) 338.70.90	Telephone No. (41-22) 338 8031

## PATENT COOPERATION TREATY

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PCT

NOTIFICATION OF THE RECORDING  
OF A CHANGE(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

TSANG, Y., Grace  
SHELL OIL COMPANY  
One Shell Plaza  
P.O. Box 2463  
Houston, TX 77252-2463  
United States of America

Date of mailing (day/month/year) 03 January 2005 (03.01.2005)	
Applicant's or agent's file reference TH2244-PCT	IMPORTANT NOTIFICATION
International application No. PCT/US2003/027995	International filing date (day/month/year) 05 September 2003 (05.09.2003)

1. The following indications appeared on record concerning:		
<input checked="" type="checkbox"/> the applicant	<input checked="" type="checkbox"/> the inventor	<input type="checkbox"/> the agent <input type="checkbox"/> the common representative
Name and Address	State of Nationality US	State of Residence US
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	
2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:		
<input checked="" type="checkbox"/> the person	<input type="checkbox"/> the name	<input type="checkbox"/> the address <input type="checkbox"/> the nationality <input type="checkbox"/> the residence
Name and Address MIGLIN, Maria, Therese 23314 Grand Springs Drive Katy, TX 713203 United States of America	State of Nationality US	State of Residence US
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	
3. Further observations, if necessary: The person identified in Box 2 is an applicant/inventor for us only.		
4. A copy of this notification has been sent to:		
<input checked="" type="checkbox"/> the receiving Office	<input type="checkbox"/> the designated Offices concerned	
<input type="checkbox"/> the International Searching Authority	<input checked="" type="checkbox"/> the elected Offices concerned	
<input checked="" type="checkbox"/> the International Preliminary Examining Authority	<input type="checkbox"/> other:	
The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland		Authorized officer Olivia TEFY (fax 338-7090)
Facsimile No. (41-22) 338.70.90		Telephone No. (41-22) 338 8516

## PATENT COOPERATION TREATY

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PCT

NOTIFICATION OF THE RECORDING  
OF A CHANGE(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

SHELL INTERNATIONAL B.V.  
Intellectual Property Services  
P.O. Box 384  
NL-2501 CJ The Hague  
Netherlands

Date of mailing (day/month/year) 04 February 2005 (04.02.2005)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference TH2244-PCT	
International application No. PCT/US2003/027995	International filing date (day/month/year) 05 September 2003 (05.09.2003)

1. The following indications appeared on record concerning: <input type="checkbox"/> the applicant <input type="checkbox"/> the inventor <input checked="" type="checkbox"/> the agent <input type="checkbox"/> the common representative	
Name and Address TSANG, Y., Grace SHELL OIL COMPANY One Shell Plaza P.O. Box 2463 Houston, TX 77252-2463 United States of America EPO - DG 1 16. 02. 2005 (52)	State of Nationality State of Residence Telephone No. 713-241-0956 Facsimile No. 713-241-6617 Teleprinter No.
2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning: <input checked="" type="checkbox"/> the person <input type="checkbox"/> the name <input type="checkbox"/> the address <input type="checkbox"/> the nationality <input type="checkbox"/> the residence	
Name and Address SHELL INTERNATIONAL B.V. Intellectual Property Services P.O. Box 384 NL-2501 CJ The Hague Netherlands EPO - DG 1 10. 07. 2005 (52)	State of Nationality State of Residence Telephone No. +31 70 377 2567 Facsimile No. +31 70 377 6141 Teleprinter No.
3. Further observations, if necessary:	
4. A copy of this notification has been sent to: <input checked="" type="checkbox"/> the receiving Office <input type="checkbox"/> the designated Offices concerned <input type="checkbox"/> the International Searching Authority <input checked="" type="checkbox"/> the elected Offices concerned <input checked="" type="checkbox"/> the International Preliminary Examining Authority <input type="checkbox"/> other:	

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. (41-22) 338.70.90	Authorized officer François BAECHLER (fax 338-7090) Telephone No. (41-22) 338 9544
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## PATENT COOPERATION TREATY

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PCT

NOTIFICATION OF THE RECORDING  
OF A CHANGE(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

SHELL INTERNATIONAL B.V.  
Intellectual Property Services  
P.O. Box 384  
NL-2501 CJ The Hague  
NetherlandsDate of mailing (day/month/year)  
04 February 2005 (04.02.2005)Applicant's or agent's file reference  
TH2244-PCT

## IMPORTANT NOTIFICATION

International application No.  
PCT/US2003/027995International filing date (day/month/year)  
05 September 2003 (05.09.2003)

## 1. The following indications appeared on record concerning:

☒ the applicant ☐ the inventor ☐ the agent ☐ the common representative

## Name and Address

SHELL OIL COMPANY  
Department of Intellectual Property  
One Shell Plaza  
P.O. Box 2463  
Houston, TX 77252-2463  
United States of America

## State of Nationality

US

## State of Residence

US

## Telephone No.

713-241-0956

## Facsimile No.

713-241-6617

## Teleprinter No.

## 2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☒ the person ☒ the name ☒ the address ☒ the nationality ☒ the residence

## Name and Address

SHELL INTERNATIONALE RESEARCH  
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Netherlands

## State of Nationality

NL

## State of Residence

NL

## Telephone No.

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## Facsimile No.

+31 70 377 6141

## Teleprinter No.

## 3. Further observations, if necessary:

The person identified in Box 2 has been recorded as applicant for all designated States  
except the United States of America.

## 4. A copy of this notification has been sent to:

☒ the receiving Office ☐ the designated Offices concerned  
☐ the International Searching Authority ☒ the elected Offices concerned  
☒ the International Preliminary Examining Authority ☐ other:The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

## Authorized officer

François BAECHLER (fax 338-7090)

Facsimile No. (41-22) 338.70.90

Telephone No. (41-22) 338 9544